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SCIENCE

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CONTENTS

<i>Address of the President to the Section of Mathematical and Physical Science of the British Association for the Advancement of Science: PROFESSOR F. T. TROUTON</i>	457
<i>The Spirit of a University: DR. MARTIN H. FISCHER</i>	464
<i>Appropriations for the Department of Agriculture</i>	471
<i>The Panama Exposition</i>	477
<i>The Franklin Medal</i>	477
<i>Scientific Notes and News</i>	478
<i>University and Educational News</i>	481
<i>Discussion and Correspondence:—</i>	
<i>The Carnegie Foundation for Teachers: DR. A. F. BLAKESLEE. Jones's A New Era of Chemistry: PROFESSOR JAS. LEWIS HOWE. Incomes of College Graduates Ten and Fifteen Years after Graduation: PROFESSOR HERBERT ADOLPHUS MILLER.</i>	483
<i>Scientific Books:—</i>	
<i>Ames on The Constitution of Matter: PROFESSOR R. A. MILLIKAN. Murray on the Chemistry of Cattle-feeding and Dairying: E. B. FORBES.</i>	485
<i>Scientific Journals and Articles</i>	487
<i>Special Articles:—</i>	
<i>Vitality and Injury as Quantitative Conceptions: PROFESSOR W. J. V. OSTERHOUT. Soil Acidity and Methods for its Detection: J. E. HARRIS. The Stark-Electric Effect: DR. GORDON S. FULCHER</i>	488

ADDRESS OF THE PRESIDENT TO THE SECTION OF MATHEMATICAL AND PHYSICAL SCIENCE OF THE BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE¹

WE have lost since the last meeting of the section several distinguished members who have in the past added so much to the usefulness of our discussions. These include Sir Robert Ball, who was one of our oldest attendants, and was president of the section at the Manchester meeting in 1886; Professor Poynting, who was President of the Section at Dover in 1899, and Sir David Gill, who was President of the Association at Leicester in 1907.

It seems appropriate at this meeting in the city of Melbourne to mention one who passed away from his scientific labors somewhat previous to the last meeting. I allude to W. Sutherland, of this city, whose writings have thrown so much light on molecular physics and whose scientific perspicacity was only equaled by his modesty.

This meeting of the British Association will be a memorable one as being indicative, as it were, of the scientific coming of age of Australia. Not that the maturity of Australian science was unknown to those best able to judge, indeed the fact could not but be known abroad, for in England alone there are many workers in science hailing from Australia and New Zealand, who have enhanced science with their investigations and who hold many important scientific posts in that country. In short, one finds it best nowadays to ask of any young investigator if he comes from the Antipodes.

MSS. intended for publication and books, etc., intended for review should be sent to Professor J. McKeen Cattell, Garrison-on-Hudson, N. Y.

¹ Section A: Australia, 1914.

This speaks well for the universities and their staffs, who have so successfully set the example of scientific investigation to their pupils.

Radioactivity and kindred phenomena seem to have attracted them most of late years, and it would perhaps have been appropriate to have shortly reviewed in this address our knowledge in these subjects, to which the sons of Australasia have so largely contributed.

Twenty-five years ago FitzGerald and others were speculating on the possibility of unlocking and utilizing the internal energy of the atom. Then came the epoch-making discovery of Becquerel, to be followed by the brilliant work of Rutherford and others showing us that no key was required to unlock this energy; the door lay open.

We have still facing us the analogous case of a hitherto untapped source of energy arising from our motion through the ether. All attempts, it is true, to realize this have failed, but nevertheless he would be a brave prophet who would deny the possibility of tapping this energy despite the ingenious theories of relativity which have been put forward to explain matters away. There is no doubt but that up to the present nothing hopeful has been accomplished towards reaching this energy and there are grave difficulties in the way; but "Relativity" is, as it were, merely trying to remove the lion in the path by laying down the general proposition that the existence of lions is an impossibility. The readiness with which the fundamental hypotheses of "Relativity" were accepted by many is characteristic of present-day physics, or perhaps, more correctly speaking, is an exaggerated example of it.

Such an acceptance as this could hardly be thought of as taking place half a century ago when a purely dynamical basis

was expected for the full explanation of all phenomena, and when facts were only held to be completely understood if amenable to such treatment; while, if not so, they were put temporarily into a kind of suspense account, waiting the time when the phenomenon would succumb to treatment based on dynamics.

Many things, perhaps not the least among them radio-activity, have conspired to change all this and to produce an attitude of mind prepared to be content with a much less rigid basis than would have been required by the natural philosophers of a past generation. These were the sturdy protestants of science, to use an analogy, while we of the present day are much more catholic in our scientific beliefs, and in fact it would seem that nowadays to be used to anything is synonymous with understanding it.

Leaving, however, these interesting questions, I will confine my remarks to a rather neglected corner of physics, namely, to the phenomena of absorption and adsorption of solutions. The term adsorption was introduced to distinguish between absorption which takes place throughout the mass of the absorbing material and those cases in which it takes place only over its surface. If, for instance, glass, powdered so as to provide a large surface, is introduced into a solution of a salt in water, we have in general some of the salt leaving the body of the solution and adhering in one form or other to the surface of the glass. It is to this the term adsorption has been applied. Physicists have now begun to take up the question seriously, but it was to biologists and especially physiological chemists that most of our knowledge of the subject in the past was due, the phenomenon being particularly attractive to them, seeing that so many of the processes they are interested in take place across surfaces.

As far as investigations already made go, the laws of adsorption appear to be very complicated, and no doubt many of the conflicting experimental results which have been obtained are in part due to this, workers under somewhat different conditions obtaining apparently contradictory effects.

On the whole, however, it may be said that the amount adsorbed increases with the strength of solution according to a simple power law, and diminishes with rise of temperature; but there are many exceptions to these simple rules. For instance, in the case of certain sulphates and nitrates the amount adsorbed by the surface of, say, precipitated silica, only increases up to a certain critical point as the strength of the solution is increased. Then further increase in the strength of the solution causes the surface to give up some of the salt it has already adsorbed or the amount adsorbed is actually less now than that adsorbed from weaker solutions. Beyond this stage for still greater concentrations of the solutions the amount adsorbed goes on increasing as before the critical point was reached.

There is some reason for thinking that there are two modes in which the salt is taken up or adsorbed by the solid surface. The first of them results from a simple strengthening of the solution in the surface layers; the second, which takes place with rather stronger concentrations, is a deposition in what is apparently analogous to the solid form. It would seem that the first reaches out from the solid surface to about 10^{-8} cm.—which is the order of the range of attraction of the particles of the solid substance.

The cause of the diminution in the adsorption layer at a certain critical value of the concentration is difficult to understand. Something analogous has been observed by

Lord Rayleigh in the thickness of layers of oil floating on the surface of water. As oil is supplied the thickness goes on increasing up to a certain point, beyond this, on further addition of oil, the layer thins itself at some places and becomes much thicker at others, intermediate thicknesses to these being apparently unstable and unable to exist. As helping towards an explanation of the diminution in the adsorption layer we may suppose that as the strength of the solution is increased from zero, the adsorption is at first merely an increased density of the solution in the surface layer. For some reason, after this has reached a certain limit, further addition of salt to the solution renders this mode of composition of the surface layers unstable, and there is a breaking up of the arrangement of the layer with a diminution in its amount. We may now suppose the second mode of deposition to begin to show its effect with a recovery in the amount of the surface layers and a further building up of the adsorption deposits.

On account of passing through this point of instability the process is irreversible, so that the application of thermo-dynamics to the phenomenon of adsorption is necessarily greatly restricted in its usefulness.

A possible cause of the instability in the adsorption layer which occurs at the critical point may be looked for in the alternations in the sign of the mutual forces between attracting particles of the kind suggested by Lord Kelvin and others. Within a certain distance apart—the molecular range—the particles of matter mutually attract one another, while at very close distances they obviously must repel, for two particles refuse to occupy the same space. At some intermediate distances the force must pass through zero value. It has for various reasons been thought that, in

addition, the force has zero value at a second distance lying between the first zero and the molecular range, with accompanying alternations in the sign of the force. Thus, starting from zero distance apart of the particles, the sign of the force is negative or repulsive; then, as the distance apart is supposed to increase, the force of repulsion diminishes, and after passing through zero value becomes positive or attractive; next, as the distance is increased the force diminishes again, and after passing through a second zero becomes negative for a second time; finally, the force on passing through a third zero becomes positive, and is then in the stage dealt with in capillary and other questions.

As an instance, of where these alternations of sign seem to be manifest, may be mentioned the case of certain crystals when split along cleavage planes. The split often runs along further than the position of the splitting instrument or inserted wedge seems to warrant. This would occur if the particles on either side of the cleavage plane were situated at the distance apart where the force between them was in the first attractive condition, for then on increasing the distance between the particles by means of the wedge the force changes sign and becomes repulsive, thus helping the splitting to be propagated further out.

Assuming that a repulsive force can supervene between the particles in the adsorption layer, through the particles becoming so crowded in places as to reduce their mutual distances to the stage when repulsion sets in, we might expect that an instability would be set up.

As already stated, a rise in temperature reduces in general the amount adsorbed, but below the critical point the nitrates and sulphates are exceptional, for rise in

temperature here increases the amount adsorbed from a given solution. This obviously necessitates that the isothermals cross one another at the critical point in an adsorption-concentration diagram. This may perhaps account for some observers finding that adsorption did not change with temperature. We have another exception to the simple laws of adsorption in the case of the alkali chlorides; this exception occurs under certain conditions of temperature and strength of solution. The normal condensation into the surface layer is reversed and the salt is repelled into the general solution instead of being attracted by the surface. In other words, it is the turn of the other constituent of the solution, namely, the water, to be adsorbed.

It is a very well known experiment in adsorption to run a solution such as that of permanganate of potash through a filter of sand, or, better, one of precipitated silica, so as to provide a very large surface. The first of the solution to come through the filter has practically lost all its salt, owing to having been adsorbed by the surface of the sand.

I was interested in finding a few months ago that Defoe, the author of "Robinson Crusoe," in one of his other books, depicts a party of African travelers as being saved from thirst in a place where the water was charged with alkali by filtering the water through bags of sand. Whether this is a practical thing or not is doubtful, or even if it has ever been tried; for it is only the first part of the liquid to come through the filter which is purified, and very soon the surface has taken up all the salt it can adsorb, and after that, of course, the solution comes through intact. It is interesting, however, to know that so long ago as Defoe's time the phenomenon of adsorption from salt solutions had been observed. It is not so well known that in the case of

some salts under the circumstances mentioned above, the first of the solution to come through the sand filter is stronger instead of weaker. This, as already mentioned, is because water, or at least a weaker solution, forms the adsorption layer.

Most of the alkali chlorides as the temperature is raised show this anomalous adsorption, provided the strength of the solution is below a certain critical value differing for each temperature. For strengths of solution above these values the normal phenomenon takes place.

No investigations seem to have been made on the effect of pressure on adsorption. These data are much to be desired.

The investigation of adsorption and absorption should throw light on osmosis, as in the first place the phenomenon occurs across a surface necessarily covered with an adsorption layer, and in the second place, as we shall see, the final condition is an equilibrium between the absorption of water by the solution and that by the membrane.

The study of the conditions of absorption of water throughout the mass of the colloidal substance of which osmotic membranes are made is of much interest. Little work has been done on the subject as yet, but what little has been done is very promising.

It is convenient to call the material of which a semi-permeable membrane is made the semi-permeable medium. The ideal semi-permeable medium will not absorb any salt from the solution, but only water, but such perfection is probably seldom to be met with. If a semi-permeable medium such as parchment paper be immersed in a solution, say, of sugar, less water is taken up or absorbed than is the case when the immersion is in pure water. The diminution in the amount absorbed is found to in-

crease with the strength of the solution. It is at the same time found that the absorption or release of water by the semi-permeable medium according as the solution is made weaker or stronger is accompanied by a swelling or shrinkage greater than can be accounted for by the water taken up or rejected.

The amount of water absorbed by a semi-permeable medium from a solution is found by experiment to depend upon the hydrostatic pressure. If the pressure be increased the amount of water absorbed by the semi-permeable medium is increased. It is always thus possible by the application of pressure to force the semi-permeable medium to take up from a given solution as much water as it takes up from pure water at atmospheric pressure.

It is not possible for a mass of such a medium to be simultaneously in contact and in equilibrium with both pure water and with a solution all at one and the same pressure, seeing that the part of the medium in contact with the pure water would hold more water than that part in contact with the solution, and consequently diffusion would take place through the mass of the medium.

If, however, the medium be arranged so as to separate the solution and the water and provided the medium is capable of standing the necessary strain, it is possible to increase the pressure of the solution without increasing the pressure of the water on the other side. Thus the part of the medium which is in contact with the solution is at a higher pressure than that part in contact with the pure solvent; consequently the medium can be in equilibrium with both the solution and the solvent, for if the pressures are rightly adjusted the moisture throughout the medium is everywhere the same.

The ordinary arrangement for showing

osmotic pressure is a case such as we are considering, and equilibrium throughout the membrane is only obtained when the necessary difference in pressure exists between the two sides of the membrane.

This condition would eventually be reached no matter how thick the membrane was. It is sometimes helpful to think of the membrane as being very thick. It precludes any temptation to view molecules as shooting across from one liquid to the other through some kind of peepholes in the membrane.

The advantage in a thin membrane in practise is simply that the necessary moisture is rapidly applied to the active surface, thus enabling the pressure on the side of the solution to rise quickly, but it has no effect on the ultimate equilibrium.

As far as that goes, the semi-permeable membrane or saturated medium might be infinitely thick, or, in other words, there need be no receptacle or place for holding the pure solvent outside the membrane at all. In fact, the function of the receptacle containing the pure solvent is only to keep the medium moist, and is no more or no less important than the vessel of water supplied to the gauze of the wet-bulb thermometer. It is merely to keep up the supply of water to the medium.

The real field where the phenomenon of osmosis takes place is the surface of separation between the saturated semi-permeable medium and the solution. Imagine a large mass of colloidal substance saturated with water and having a cavity containing a solution. The pressure will now tend to rise in the cavity until it reaches the osmotic pressure—that is, until there is established an equilibrium of surface transfer of molecules from the solution into the medium and back from the medium into the solution.

No doubt, the phenomenon as thus de-

scribed occurs often in nature. It is just possible that the high-pressure liquid cavities, which mineralogists find in certain rock crystals, have been formed in some such manner in the midst of a mass of semi-permeable medium; the pure solvent in this case being carbon dioxide and the medium colloidal silica, which has since changed into quartz crystal.

In considering equilibrium between a saturated semi-permeable medium and a solution there seems to me to be a point which should be carefully considered before being neglected in any complete theory. That is, the adsorption layer over the surface of the semi-permeable medium. We have seen that solutions are profoundly modified in the surface layers adjoining certain solids, through concentration or otherwise of the salts in the surface layer, so that the actual equilibrium of surface transfer of water molecules is not between the unmodified solution and the semi-permeable medium, but between the altered solution in the absorption layer and the saturated medium. Actual determinations of the adsorption by colloids are much wanted, so as to be able to be quite sure of what this correction amounts to or even if it exists. It may turn out to be zero. If there is adsorption, however, it may possibly help to account for part of the unexpectedly high values of the osmotic pressure observed at high concentrations of the solution, the equilibrium being, as we have seen, between the saturated medium and a solution of greater concentration than the bulk of the liquid, namely, that of the adsorption layer. In addition, when above the critical adsorption point, there may be a deposit in the solid state. This may produce a kind of polarized equilibrium of surface transfer in which the molecules which discharge from the saturated medium remain unaltered in amount, but those

which move back from the adsorption layer are reduced owing to this deposit, thus necessitating an increase in pressure for equilibrium. If either or both of these effects really exist, it would seem to require that the pressure should be higher for equilibrium of the molecular surface transfer than if there were no adsorption layer and the unaltered solution were to touch the medium, but at the same time it should be remembered that there is a second surface where equilibrium must also exist—that is, the surface of separation of the adsorption layer and the solution itself. It is just possible that the two together cancel each other's action.

Quantitative determinations of adsorption by solid media from solution are hard to carry out, but with a liquid medium it is not so difficult. Ether constitutes an excellent semi-permeable medium for use with sugar solution, because it takes up or dissolves only a small quantity of water and no sugar. A series of experiments using these for medium and solution has shown (1) that the absorption of water from a solution diminishes with the strength of the solution; and (2) that the absorption of water for any given strength of solution increases with the pressure. This increase with pressure is somewhat more rapid than if it were in proportion to the pressure. On the other hand, from pure water ether absorbs in excess of normal almost in proportion to the pressure. Certainly this is so up to 100 atmospheres. This would go to confirm the suggestion already made that the departure from proportionality in the osmotic pressure is attributable to absorption.

By applying pressure ether can be thus made to take up the same quantity of water from any given solution as it takes up from pure water at atmospheric pressure. It is found by experiment that this pressure is

the osmotic pressure proper to the solution in question.

Decidedly the most interesting fact connected with the whole question of osmotic pressure, the behavior of vapor pressures from solution, and the equilibrium of molecular transfer of solutions with colloids, is that discovered by Van't Hoff, that the hydrostatic pressure in question is equal to what would be produced by a gas having the same number of particles as those of the introduced salt. Take the case of a mass of colloid or semi-permeable medium placed in a vessel of water; the colloid when in equilibrium at atmospheric pressure holds what we will call the normal moisture. By increasing the pressure this moisture can be increased to any desired amount. Now, on introducing salt the moisture in the colloid can be reduced at will. The question is, what quantity of salt must be introduced just to bring back the amount of the moisture in the colloid to normal? Here we get a great insight into the internal mechanism of the liquid state. The quantity of salt required turns out to be, approximately at least, that amount which if in the gaseous state would produce the pressure. So that normality can be either directly restored by removing the pressure or indirectly by introducing salt in quantity which just takes up the applied pressure. That this is so naturally suggested that the salt, although compelled to remain within the confines of the liquid, nevertheless produces the same molecular bombardment as it would were it in the gaseous state, though of course the free path must be viewed as enormously restricted compared with that in the gaseous state.

Many have felt a difficulty in accepting this view of a molecular bombardment occurring in the liquid state, but of recent years much light has been thrown on the subject of molecular movements in liquids,

especially by Perrin's work, so that much of the basis of this difficulty may be fairly considered as now removed.

Quite analogous to the reduction from the normal of the moisture held by a semi-permeable medium brought about by the addition of salt to the water, is the reduction in the vapor pressure arising from the presence of a salt in the water. The vapor pressure is likewise increased by the application of hydrostatic pressure, which may be effected by means of an inert gas. In both cases the hydrostatic pressure which must be applied to bring back to normality is equal to that which the added salt would exert if it were in the state of vapor or, in other words, the osmotic pressure.

The two cases are really very similar. In both there is equal molecular transfer backwards and forwards across the bounding surface. In the one a transfer from that solution to the semi-permeable medium and back from it into the solution. In the other a transfer from the solution into the superambient vapor and back from it into the solution.

The processes are very similar, namely, equal molecular transfer to and fro across the respective surfaces of separation.

Thus we may in the case of osmotic equilibrium attribute the phenomenon with Callender to evaporation, but not evaporation in its restricted sense, from a free surface of liquid, but as we have seen from a saturated colloidal surface into the solution. This process might perhaps be better referred to as molecular emigration, the term migration being already a familiar one in connection with liquid phenomena.

F. T. TROUTON

THE SPIRIT OF A UNIVERSITY

A DECADE ago in the United States of America, in a university rated among the first in numbers of students, the professor

of astronomy was summoned before the president and the governing board and asked whether he believed the nebular hypothesis which he discussed in a text-book issued under his name. An answer in the affirmative was promised to cost him his teaching position. He answered in the negative, and to prove his sincerity assented to calling in his books and having them burned in public. A less number of years ago a university president whom we to-day honor as a first citizen found it well, or shall we say necessary, to step out of his chosen field of work because he held the minority view among his associates that the word democracy does not mean a political party only. Some months ago a professor of philosophy, teaching its principles as he saw them and under a freedom apparently guaranteed him by charter, alleges his resignation is requested because such teaching in the mind of his president is incompatible with the doctrinal views of an avowedly religious organization operating in some state or states of our Union.

Again, the members of a faculty wake to their accustomed labors and over the coffee and in the newspaper receive first word that their places have over night been declared vacant; a university president demands that his faculty vote Yes or No as an expression of their confidence in him; a faculty member backed by brains and fearlessness rises to condemn most of those time-sanctified institutions of boards of control and university presidents.

It is well to emphasize that these illustrations do not represent hand-picked rarities, but are typical of a class of problems which in greater or less degree arise periodically to clog the machinery of university education. Neither can it be said that a correct solution is not usually found for them. The only question of importance is why the delay in so doing and why so much